



PATENT
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IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant: Koon Gee NEOH et al. Conf.: 9536
Appl. No.: 09/895,153 Group: 1762
Filed: July 2, 2001 Examiner: TSOY, E.
For: PHOTOINDUCED CONVERSION OF
POLYANILINE FROM AN INSULATING STATE
TO A CONDUCTING STATE

DECLARATION UNDER 37 CFR § 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450
Sir:

In connection with the above-identified U.S. Patent Application, I, Ms. Xin Liu,
hereby declare as follows:

1. I am a citizen of the Peoples' Republic of China, presently residing at Woodlands
Drive 72, Block 787D, #8-24, Singapore 734787, and receiving mail at the Department of
Chemical and Biomolecular Engineering, National University of Singapore, Block ES, #04-
07, Engineering Drive 4, Singapore 119260.

2. I have read the specification and pending claims of U.S. Patent Application
09/895,153 (hereinafter "the present application"), and also the Office Action mailed from
the USPTO on October 7, 2003.

3. In the course of study for a Ph.D. degree in the Department of Chemical and Environmental Engineering of the National University of Singapore, I undertook my thesis research in the laboratories of Professor K.G. Neoh and Professor E.T. Kang, both of whom are named as co-inventors of the present application. A copy of my Curriculum Vitae is attached as Exhibit 1.

4. I have conducted the following experiment under the supervision and at the direction of Professor Neoh and Professor Kang.

Viologen monomer, 1,1'-bis(4-vinyl-benzyl)-4,4'-bipyridinium dichloride, (VBV) was synthesized as reported in Liu, X. et al, Langmuir 18 (2002) 2914. A copy of this paper is attached as Exhibit 2.

Polyaniline (PANI) was coated onto a low density polyethylene (LDPE) film by immersing the LDPE film into a mixture of 0.1 M aniline and 0.025 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 1M HClO_4 for 2 hr. at 0 °C. The film was then washed with 1M HClO_4 for 1 hr. followed by dipping into 0.5M NaOH for 1 hr. to obtain an undoped PANI film. The PANI-coated-LDPE was then pretreated with argon plasma for 20 seconds. Graft copolymerization of VBV was then carried out by placing an aqueous solution of VBV (40 wt%) on the surface of the argon plasma pretreated PANI coated LDPE. The film was sandwiched between two quartz plates and exposed to near-UV irradiation in a Riko rotary photochemical reactor (RH400-10W) for 20 minutes. The graft copolymerized PANI coated LDPE was removed from the quartz plates after prolonged immersion in water then again subjected to thorough washing with water to remove viologen which was not graft copolymerized on the substrate.

The VBV grafted PANI coated LDPE was then irradiated with UV irradiation for 20 minutes and the conductivity was measured. UV-visible spectroscopic analysis of the film after irradiation was also performed.

The sheet resistance of the VBV-grafted, PANI-coated LDPE was greater than 10^{11} ohm/sq, which should be compared with the sheet resistance of the materials of Examples 1 and 2 of the present application, shown in Figure 1 thereof as approximately 10^6 ohm/sq and 10^5 ohm/sq, respectively. Thus, the material produced as described above has negligible conductivity in comparison to the conductivity of the inventive material of the present application.

Furthermore, the material prepared from the grafted viologen (VBV) fails to show the changes in absorbance characteristic of the conductive state. Figure 2 of the present application, a copy of which is attached hereto as Exhibit 3, shows the ultraviolet absorption spectra of the material of Example 1 of the present application over a course of 20 minutes of irradiation, during which the conductive state of the material develops. These spectra show the development of the spectral properties indicative of a highly conductive state, i.e. a disappearance of a peak at about 600 nm and the appearance of an absorption "tail" above 700 nm, after about 10 to 20 minutes of irradiation.

The attached Exhibit 4 shows absorbance spectra of the grafted viologen (VBV) product taken at various times after irradiation for 20 minutes. For purposes of this Declaration, the 0 and 35 minute time points are relevant. The reader should note that the tail indicative of the conducting state is completely absent from these spectra.

The conductivity of the material obtained by grafting viologen (VBV) directly to a PANI film is poor because of extensive cross-linking of the viologen. However, *in situ*

synthesis of the viologen avoids such cross-linking and allows the formation of a conductive material.

5. Furthermore, the present application provides evidence that the process by which the viologen salt is grown upon a substrate can influence the rate at which conductivity develops in a polymer that is oxidatively doped by a viologen salt. In Examples 1 and 2, a viologen salt is produced *in situ* upon a LDPE substrate by two different processes. In Example 1, the viologen is produced by reaction of 4,4'-bipyridine with a vinyl benzyl chloride grafted substrate film, followed by a second reaction with vinyl benzyl chloride. On the other hand, in Example 2, the viologen is produced by reaction of a vinyl benzyl chloride grafted substrate film with 4,4'-bipyridine and p-xylene dichloride. The resulting viologen-grafted substrates are then reacted in the same manner with aniline and ammonium persulfate to form a doped polyaniline.

Figure 1 shows the acquisition of conductivity versus time for the two materials upon irradiation. The reader should note that the two different processes for producing a viologen-grafted film produce materials that acquire conductivity at different rates.

6. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: March, 04, 2014

By Xin Liu

Ms. Xin Liu

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Personal Data

Date of Birth: May 1, 1976
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Education

Ph.D. Student (Jan. 2001-present)
Department of Chemical & Environmental Engineering
National University of Singapore
Supervisors: Prof. K.G. Neoh and Prof. E.T. Kang

B. Eng Student (Sept. 1994-Jul. 2000)
Department of Chemical Engineering
Tsinghua University
Major: Chemical Engineering
Supervisor: Prof. D. H. Liu
Title of Thesis: Flocculating separation of chlorotetracycline after fermentation.

Research Experience

Ph.D Research (Jan. 2001-present)
Department of Chemical & Environmental Engineering
National University of Singapore
Research Fields:

- * Surface functionalization of substrates with viologen for photoelectrical and electrochemical applications including polyethylene, silanized glass, polyaniline indium-tin oxide, gold and polypyrrole films.
- * Immobilization of glucose oxidase on electrical conductive polymer surface via viologen for application as biosensor.

- * Fabrication and modification of membrane cast from poly(vinylidene fluoride)-VBC copolymer and redox-controlled permeability study.

Practical Skills

Instrumental:	2 years experience of operating AFM, FTIR, TGA, UV-vis, EA, Auto-Lab, Optical Microscope; Familiar with XPS, TEM, laser light scattering equipment mechanism and operation; Basic electrical equipment maintenance; Theoretical and practical instrumental knowledge.
Experimental:	Organic synthesis, plasma treatment, electropolymerization, membrane fabrication.
Computer Literacy:	Use of Word, Excel, Powerpoint, Origin, ChemDraw, Photoshop, ACDsee, etc. software for writing and data analyzing; Familiar with Windows and Linux operating system; Use of the internet, webpage-building; Computer programming with Fortran and Basic.
Language:	Good communicating and writing skill in English and Chinese.
Sports & Music:	Bronze Class of International Standard Ballroom Dancing, 1994-2000 Member of Military Band of Tsinghua University, Instrument: ^b E flute, 1994-2000.

Honors

- * President Graduate Fellowship, National University of Singapore, July, 2002-present
- * Research Scholarship, National University of Singapore, Jan., 2001- present
- * Outstanding Student Award, Tsinghua University, Sep. 1998
- * Outstanding Student Award, Tsinghua University, Sep. 1996
- * Outstanding Student Award, Tsinghua University, Sep. 1995

Publications

X. Liu, K. G. Neoh, L. Zhao, and E. T. Kang Surface functionalization of glass and polymeric substrates via graft copolymerization of viologen in an aqueous medium. *Langmuir* 2002, 18, 2914-2921.

X. Liu, K. G. Neoh, and E. T. Kang Viologen-functionalized conductive surfaces: physicochemical and electrochemical characteristics, and stability. *Langmuir* 2002, 18, 9041-9047.

X. Liu, K. G. Neoh, and E. T. Kang Enzymatic activity of glucose oxidase covalently wired via viologen to electrically conductive polypyrrole films. *Biosensors and Bioelectronics* 2003 Accepted.

X. Liu, K. G. Neoh, and E. T. Kang Redox sensitive microporous membranes prepared from poly(vinylidene fluoride) grafted with viologen-containing polymer side chains. *Macromolecules* 2003, 36, 8361-8367.

X. Liu, K. G. Neoh, and E. T. Kang Synthesis and characterization of viologen containing poly (4-vinyl-benzyl-chloride)-graft-poly (vinylidene fluoride) redox-sensitive membranes. *Surface and Interface Analysis* 2003 Submitted.

Surface Functionalization of Glass and Polymeric Substrates via Graft Copolymerization of Viologen in an Aqueous Medium

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Surface functionalization of low-density polyethylene (LDPE), silanized glass, and free-standing polyaniline (PANI) films via UV-induced graft copolymerization with 1,1'-bis(4-vinyl-benzyl)-4,4'-bipyridinium dichloride (VBV) was carried out. The vinyl group containing viologen was synthesized by the double Anderson reaction using 4,4'-bipyridine and vinyl benzyl chloride and characterized by elemental analysis, FTIR spectrum, and X-ray photoelectron spectroscopy. The graft copolymerization of VBV was carried out by placing the plasma-pretreated substrate in contact with an aqueous solution of VBV under UV irradiation. The effects of the plasma-pretreatment time of the substrate, UV-induced graft copolymerization time, and monomer concentration on the VBV-graft copolymer concentration were investigated. The responses of the VBV-graft-copolymerized LDPE films and silanized glass slides to photoirradiation were monitored. In both cases, intensely blue viologen radical cations were formed after 10 min of UV irradiation in a vacuum and bleaching occurred when the substrate was exposed to air upon termination of the irradiation. VBV-graft-copolymerized PANI films with good conductivity can be prepared, and these films may have possible applications as active templates in biosensors where the viologen groups may serve as electron transfer mediators from the electrode surface to the active site of biomaterials. This method of surface functionalization of viologen moieties offers a number of advantages over a previously developed technique.

Introduction

Viologens or 1,1'-disubstituted-4,4'-bipyridinium dications are one of a group of electrochromic materials. These compounds show significant reversibility¹ and exhibit a large change in the visible extinction coefficient following reduction.^{2,3} The visual change in color may be initiated by near-UV irradiation, electrical current, or a chemical reductant.⁴ Numerous studies on 4,4'-bipyridine, its derivatives, complexes of 2, 2'-bipyridine, and ruthenium for use in electrochemical and electrochromic applications, such as modified electrodes,^{5–8} photochromic materials,^{9,10} electron-transfer membranes,¹¹ electrochromic displays,^{12,13} and amperometric glucose sensors,¹⁴ have been carried out. Many studies have also been carried out on the facile

redox reactivity and low redox potential of viologens. When copolymerized with biomaterials and conductive polymers such as polypyrrole and polyaniline,^{15,16} viologens have been demonstrated as redox mediators and electron acceptors for use in bioseparators¹⁷ and biosensors.¹⁸ However, viologen dications are generally soluble in water, and hence it is difficult to retain them on substrates for possible applications in aqueous solutions. To circumvent this problem, insoluble polymers with viologen moieties have been synthesized.^{6,19–21} Other studies have been carried out with viologens incorporated into anionic polyelectrolyte films²² and in zeolites matrixes.^{23,24} Our group and others have carried out surface modification of polymeric substrates via graft copolymerization to impart new and specific functionalities to the polymer surface,^{25–29}

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and this technique can also be employed for the immobilization of viologens.

In our previous study, the functionalization of low-density polyethylene (LDPE) film with viologen moieties²⁵ was first carried out via the UV-induced graft copolymerization of 4-vinyl benzyl chloride on the plasma-pretreated surface of the LDPE film. The pendent benzyl chloride groups on the LDPE film surface then serve as functional groups for the introduction of the viologen moiety. This viologen-LDPE system offers the advantage of being a thin flexible film that can be shaped and is suitable for large area displays. Furthermore, the thin surface layer of viologen polymer offers a rapid photochromic response. Nevertheless, this method is restricted to polymeric substrates which would be stable during prolonged reaction in organic solvents.

In the present work, we report a new method which offers several advantages in comparison with the previous method: reduction in treatment time, elimination of the use of organic solvents during surface functionalization, and enhancement of film properties. In the present work, a vinyl group containing viologen (1,1'-bis(4-vinyl-benzyl)-4,4'-bipyridinium dichloride, VBV) was first synthesized and then graft copolymerized on the substrates. Different substrates were tested, and the effects of substrate pretreatment, graft copolymerization time, and monomer concentration were evaluated. The response of the viologen-functionalized substrates to UV irradiation was also studied. The surface resistance and conductivity of viologen-functionalized electroactive polyaniline films were investigated. The pristine and graft-modified substrates were characterized using X-ray photoelectron spectroscopy (XPS), UV-vis absorption spectroscopy, and scanning electron microscopy (SEM).

Experimental Section

Materials. Low-density polyethylene (LDPE) films were purchased from Goodfellow Inc., U.K. Vinyl benzyl chloride (VBC), 4,4'-bipyridine (98%), aniline (99%), ammonium persulfate, 3-glycidypropyltrimethoxy silane (GPS), hydrogen peroxide, and sulfuric acid were obtained from Aldrich Chemical Co. and were used as received. Solvents, such as *N*-methyl-2-pyrrolidinone (NMP), acetonitrile, acetone, and other chemicals were of reagent grade and used as received from Aldrich Chemical Co.

Sample Preparation. *Synthesis of Viologen.* 1,1'-bis(4-vinyl-benzyl)-4,4'-bipyridinium dichloride was synthesized, according to the method reported in the literature,^{4,30} by the double Anderson reaction using 4.97 g (0.03 mol) of 4,4'-bipyridine and 12.5 mL (0.08 mol) of VBC in 30 mL of acetonitrile at 75 °C for 3 h. The resulting yellow precipitate was recrystallized twice from acetone to obtain a pale yellow powder of 88.7% yield. This vinyl group containing viologen will be denoted as VBV in the subsequent discussion.

Preparation of Substrates. LDPE films were cut into strips of 2 cm × 4 cm, washed in acetone for 10 min using an ultrasonic bath to remove surface impurities, and then washed with a copious amount of doubly distilled water. Glass slides were cut into strips of 1 cm × 2 cm and also washed ultrasonically in acetone for 10 min. To ensure the removal of the organic residues from the surface, the glass slides were then cleaned using the "piranha" solution (a mixture of 70% concentrated sulfuric acid and 30% hydrogen peroxide).³¹ The cleaned glass slides were

then washed with doubly distilled water and kept immersed in doubly distilled water to ensure that the slides remain wettable when aqueous silane solutions were applied.

Polyaniline (PANI) was synthesized via the oxidative polymerization of aniline with ammonium persulfate in 1 M HCl at 0 °C according to the method described in the literature.^{32,33} It was converted to emeraldine (EM) base after treatment with excess 0.5 M NaOH for 24 h, followed by washing with doubly distilled water until the filtrate was neutral. The base powder was dried under reduced pressure for 24 h. Free-standing EM base films with thickness of about 10–20 μm were prepared by casting from NMP solution containing 5 wt % of EM base. The EM base films were reprotonated by immersion in 1 M HClO₄ solution for 24 h to form EM salt films, washed with doubly distilled water, and then dried under reduced pressure for another 24 h.

Silane Treatment of the Glass Slide Surface. A 1 vol % of silane solution is used in the silanization of the glass surface. It has been reported that the deposition of silane onto glass from a 0.25 vol % solution could result in about eight molecular layers³⁴ and increasing the silane solution concentration to above 1 vol % does not cause a further increase in the multilayer thickness. A 95% ethanol–5% water solution was adjusted to pH 4.5–5.5 with acetic acid. GPS was added with stirring to yield a 1 vol % final concentration. A reaction time of 30 min was used to allow for hydrolysis and silanol formation. Glass slides were taken from storage in doubly distilled water and dipped into the solution. This procedure kept hydrocarbon contamination to minimum and ensured that the slides remained completely wettable when immersed in the aqueous silane solution. The glass slides were removed after 10 min. They were rinsed free of excess material by dipping briefly in ethanol. Curing of the silane layer was carried out for 1 h at 100 °C in an oven. The surface-modified glass slides were then washed with a copious amount of doubly distilled water and dried under reduced pressure.

Plasma Treatment. Argon plasma pretreatment of the cleaned LDPE films, the silanized glass slides, and EM films were carried out in an Anatech SP100 plasma system, equipped with a cylindrical quartz reactor chamber. The glow discharge was produced at a plasma power of 35 W, an applied oscillator frequency of 40 kHz, and an argon pressure of approximately 0.6 Torr. These plasma-pretreated substrates were then exposed to air for 5–10 min to facilitate the formation of surface oxide and peroxide groups before graft copolymerization was carried out.³⁵

UV-Induced Surface Graft Polymerization. An aqueous solution of the viologen monomer was placed on the surface of the argon plasma-pretreated substrate which was sandwiched between two pieces of quartz plates. Different monomer concentrations ranging from 12.5 to 40 wt % were tested. The assembly was exposed to near-UV irradiation in a Riko rotary photochemical reactor (RH400-10W) for different periods of time. The reactor was equipped with a 1000 W high-pressure Hg lamp and a constant temperature water bath. All the UV-induced graft polymerization experiments were carried out at a constant temperature of 28 °C. The graft-copolymerized substrate was extracted from the quartz plates after prolonged immersion in water and then again subjected to thorough washing with water to remove viologen which was not graft copolymerized on the substrates. An overall scheme of the silanization, argon plasma-pretreatment steps, and the graft copolymerization of viologen with the various substrates is shown in Scheme 1.

Testing and Characterization. The as-synthesized VBV powder was mixed with KBr to make the test pellet specimens for FTIR analysis using a BIO-RAD FTS 135 spectrophotometer. Its bulk chemical composition was analyzed using a Perkin-Elmer model 2400 CHN elemental analyzer. The total bulk Cl content was determined by the Schöniger combustion method in which

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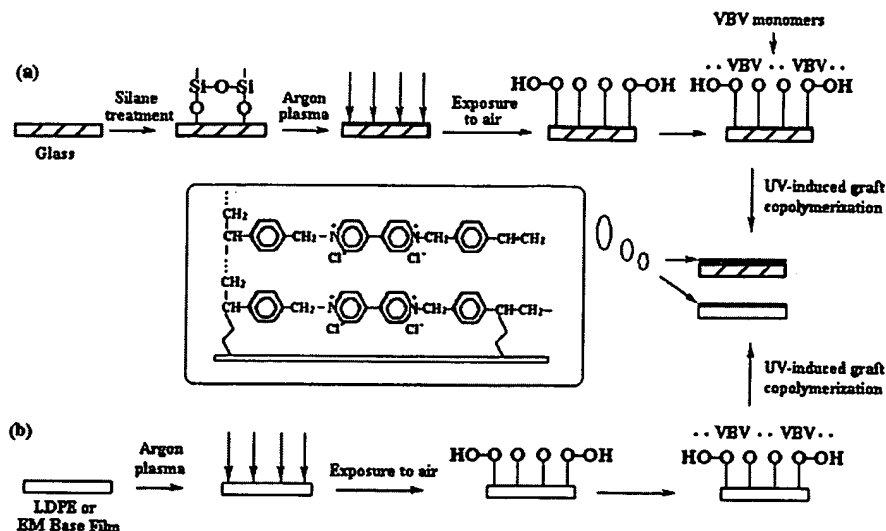
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Scheme 1



the chemical titration was carried out using mercuric(II) nitrate.³⁶ The response of the viologen functionalized substrates to UV irradiation was performed at a temperature between 24 and 28 °C, using a 1 kW Hg lamp in the Riko rotary reactor. The samples were placed in Pyrex tubes and positioned 5 cm from the light source. In the experiments requiring the absence of air, the samples were placed in an evacuated quartz cell. The UV-vis absorption of the films before and after irradiation was monitored on a Shimadzu UV-3101 PC scanning spectrophotometer, using the pristine (untreated) substrate as the reference.

Surface compositions were measured using XPS on an AXIS HSi spectrometer with an Al K α X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV. The anode voltage was 15 kV and the anode current was 10 mA. The pressure in the analysis chamber was maintained at 5.0×10^{-8} Torr or lower during each measurement. The substrates were mounted on the standard sample studs by means of double-sided adhesive tape. The core-level signals were obtained at a photoelectron takeoff angle of 90° (with respect to the sample surface). All binding energies (BEs) were referenced to the C 1s hydrocarbon peak at 284.6 eV. In the peak synthesis, the line width (full width at half-maximum) of the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental components were determined from peak area ratios corrected with the experimentally determined sensitivity factors and were reliable to $\pm 5\%$. The two probe technique was used to measure the surface resistance (R_s in Ω/sq) of the film (conductivity = $1/(R_s \times \text{thickness of the film})$).³⁷ For each surface resistance value reported, at least three sample measurements were averaged. The conductivity of EM films was also measured using a four-point probe (Singaton Corp.).³⁸ The conductivities of the films were calculated from the measurements of the voltage under controlled current applied to the film using the equations derived by Van der Pauw.³⁸ A comparison of the conductivities calculated from the surface resistances of a number of films and the conductivities of the corresponding films as measured by the four-probe technique was carried out. For the more conductive films ($R_s \approx 10^3 \Omega/\text{sq}$), the two values are generally within a factor of 2. The R_s measurements were used in this work to provide the means for comparing the surface conductivity changes of the films under various experimental conditions while conductivity values were reported for the more conductive films.

SEM was carried out on a JEOL, JSM 5600LV scanning electron microscope. The samples were cleaned with an inert

Table 1. Elemental Analysis of As-Synthesized VBV Powder

	elemental content (wt %)	
	experimental	theoretical (based on $\text{C}_{28}\text{H}_{26}\text{N}_2\text{Cl}_2$)
C	71.39	72.83
H	5.89	5.63
N	6.19	6.07
Cl	14.43	15.39

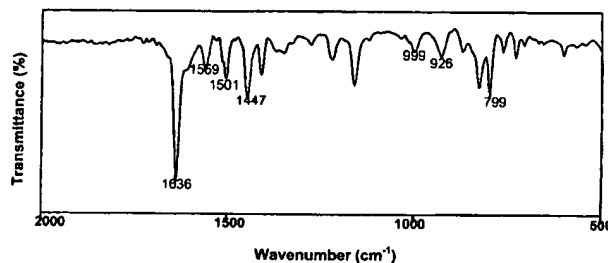


Figure 1. FTIR spectrum of as-synthesized VBV powder.

dusting gas and sputter-coated with a thin film of platinum for imaging purposes. Images were taken at 15 kV at a magnification of $\times 10\,000$.

Results and Discussion

1. Properties of Viologen Monomer (VBV). The elemental analysis of the as-synthesized VBV monomer is shown in Table 1. The results compare well with the theoretical values expected for $\text{C}_{28}\text{H}_{26}\text{N}_2\text{Cl}_2$. The FTIR spectrum of VBV is shown in Figure 1. The absorption bands at 1559 and 1447 cm^{-1} are attributed to the C-H stretching of 4-substituted pyridine while the absorption band at 1636 cm^{-1} is due to a combination of C-H and $\text{C}=\text{N}$ stretching.^{4,39,40} The absorption bands at 1501 and 799 cm^{-1} have been associated with 1,4-disubstituted benzene ring C-H stretching and the two adjacent hydrogen diagnostic bands.⁴¹ The presence of the absorption peaks at 926 and 999 cm^{-1} in Figure 1 are attributed to CH_2 wag and trans CH in-phase wag of the vinyl group,⁴¹

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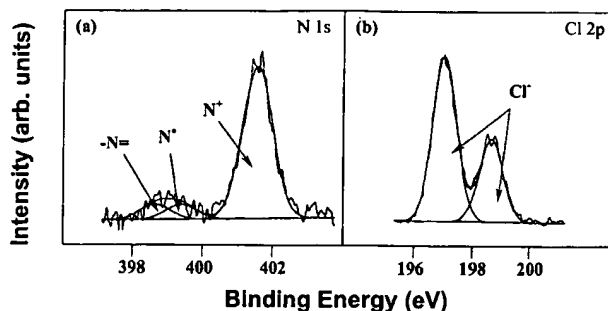


Figure 2. XPS: (a) N 1s and (b) Cl 2p core-level spectra of as-synthesized VBV powder.

the presence of which ensures the possibility of the subsequent graft copolymerization with the substrates. The results from the elemental and FTIR analysis of the as-synthesized VBV monomer are thus consistent with those of the expected 1,1'-bis(4-vinyl-benzyl)-4,4'-bipyridinium dichloride.

The XPS N 1s and Cl 2p core-level spectra of the as-synthesized VBV are shown in Figure 2. The N 1s core-level spectrum of VBV can be fitted with three peaks. The peak at 401.7 eV is assigned to the positively charged nitrogen (N^+), that at 399.5 eV is attributed to the viologen radical cation (N^\bullet) formed during X-ray excitation in the analysis chamber,²³ and finally the peak at 398.6 eV is assigned to the unreacted imine nitrogen ($-N=$) of the pyridine rings.⁴² The Cl 2p core-level spectrum of VBV is deconvoluted into a spin-orbit split doublet with the binding energies for the $Cl\ 2p_{3/2}$ and $Cl\ 2p_{1/2}$ component peaks at 197.1 and 198.6 eV, which is attributable to ionic Cl (Cl^-).⁴³ As shown in Figure 2, the positively charged nitrogen (N^+) is the dominant feature which indicates that the 4,4'-bipyridine has been mostly diquaternized during the synthesis step. The $[N^+]/[Cl^-]$ ratio is 1.04, which is expected if charge neutrality is to be maintained.

2. VBV-Graft Copolymerization on LDPE. Figure 3 shows the XPS wide-scan N1s and Cl 2p core-level spectra of the VBV-graft-copolymerized LDPE surface (20 s plasma pretreatment, 40 wt % VBV in water, 20 min UV irradiation). From the wide-scan spectrum (Figure 3a), the presence of N and Cl groups can be clearly seen, indicating that VBV has been successfully graft copolymerized on the LDPE surface. The N 1s core-level spectrum (Figure 3b) can be fitted with three peak components in a similar manner as that used in Figure 2a. Similarly, the Cl exists predominantly in the ionic state (Figure 3c) similar to that shown in Figure 2b. An indication of the approximate amount of VBV graft copolymerized on the LDPE surface can be inferred from the $[N]/[C]$ ratio. In the case shown in Figure 3 (20 s plasma pretreatment, 20 min UV-induced graft copolymerization, and 40% VBV monomer), the $[N]/[C]$ ratio calculated from the XPS analysis is 0.07, which is expected of VBV (2N and 28C), and the $[N^+]/[Cl^-]$ ratio is 1.06. When the VBV monomer concentration is decreased to 30 or 20 wt % under same plasma and UV treatment conditions, the $[N]/[C]$ ratio from the XPS analysis remains at 0.07, even though the yellow color of the films become less intense at lower VBV concentration, which suggests less viologen moieties are graft copolymerized on the surface. The XPS technique is highly surface sensitive (probing depth ~ 10 nm), and

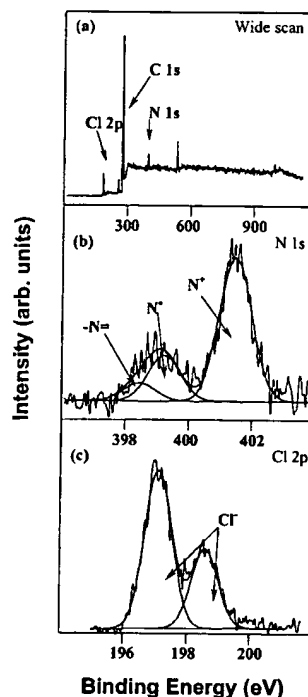


Figure 3. XPS: (a) wide scan, (b) N1s, and (c) Cl 2p core-level spectra of VBV-graft-copolymerized LDPE film. Graft copolymerization is carried out with 20 s plasma pretreatment, 20 min UV irradiation, and 40 wt % VBV in water.

hence once the graft layer on the LDPE surface is thicker than the probing depth, a further increase in the amount of VBV-graft copolymerized on the LDPE surface would not result in further changes in the $[N]/[C]$ ratio. A 12.5 wt % VBV solution was also attempted, but this concentration was too low to result in a homogeneously VBV-graft-copolymerized surface. The UV-vis absorption spectroscopy technique would give a better indication of the amount of VBV-graft copolymerized on the LDPE surface and will be discussed in a later section.

The effects of argon plasma-pretreatment time and UV-irradiation time on the graft concentration of the VBV-graft-copolymerized films are shown in Figure 4. An increase in the argon plasma-pretreatment time from 10 to 20 s results in more activated sites on the substrate, which in turn leads to the formation of more peroxide and hydroperoxide species (upon exposure to air) for the subsequent UV-induced surface graft polymerization. However, the graft concentration shows a slight decrease with further increase in argon plasma-treatment time beyond 20 s. It has been reported previously that intensive cross-linking of the polymer radicals upon prolonged plasma treatment may decrease the amount of radicals available for peroxide formation when the substrate is subsequently exposed to air.³⁵ Furthermore, it has also been reported that the active species formed initially on the LDPE surface can be partially removed by the etching effects of the plasma upon increasing the plasma-treatment time.³¹ Thus, the results in Figure 4 indicate that the optimum graft concentration is obtained after an argon plasma-pretreatment time of 20 s.

Figure 4 also shows that UV graft polymerization time in the range from 10 to 60 min does not have a substantial effect on the graft concentration of VBV on the LDPE films. With an argon pretreatment time of 20 s, a UV-irradiation time of 20 min is adequate to achieve a graft layer of at least 10 nm. Prolonged UV-irradiation time

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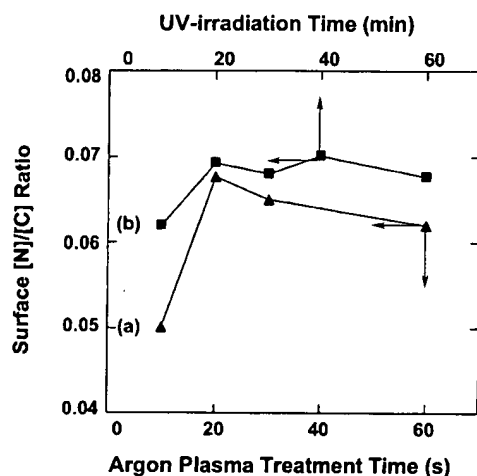


Figure 4. N/C ratio as determined by XPS of VBV-graft-copolymerized LDPE films with (a) different periods of argon plasma-treatment time and 60 min of UV-induced graft copolymerization time and (b) 20 s of argon plasma-treatment time and different periods of UV-induced graft copolymerization time.

may result in the side reaction of the pyridine species. On the basis of the observed effects of argon plasma-pretreatment time and UV graft polymerization time on the graft concentration, the VBV-graft-copolymerized LDPE films prepared under the optimum conditions of 20 s of argon plasma-pretreatment time and 20 min of UV graft polymerization time were used for the subsequent tests discussed below.

The response of the VBV-graft-copolymerized LDPE films to photoirradiation and their subsequent bleaching in air were monitored by UV-vis absorption spectroscopy. The UV-vis spectra of VBV-graft-copolymerized LDPE films before and after UV irradiation are compared in Figure 5 a. The "base" spectrum is that of the film before irradiation, and no absorption bands are seen in the range of 400–800 nm. The "0 min" spectrum denotes the spectrum of the film after 10 min of irradiation using the 1 kW Hg lamp in a vacuum. There are two peaks at 615 and 407 nm which indicate the formation of viologen radical cations.^{44,45} After the 10 min irradiation period, the film is exposed to air and allowed to bleach in the dark. In the presence of air, the reaction of the viologen radical cations with O₂ regenerates the viologen dication and this reaction has been known to be particularly fast because of the strong reductive ability of the viologen radical cation.⁴⁶ It results in the decrease of the intensities of the absorption bands at 615 and 407 nm. The spectrum of the film eventually approaches the base spectrum when all radical cations are converted back to the dications. These changes in the viologen-grafted LDPE films upon irradiation can also be followed visually as the films change from pale yellow to blue upon irradiation and the blue coloration fades as the films are exposed to air.

The amount of VBV grafted on the films affects the response to irradiation, as well as the bleaching. The response of the films prepared by using VBV solutions of 40, 30, and 20 wt % (films A, B, C, respectively) is shown in Figure 6a. The relative absorbance of the film is calculated as the absolute absorbance at any one time

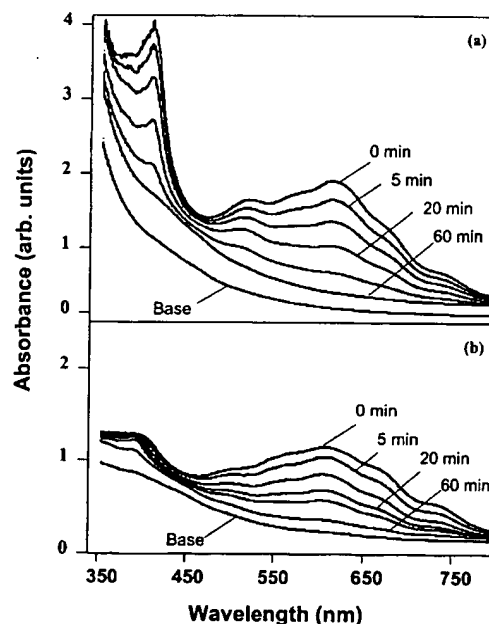


Figure 5. UV-vis absorption spectra of (a) VBV-graft-copolymerized LDPE film and (b) VBV-graft-copolymerized silanized glass, irradiated and bleached in air. Graft copolymerization is carried out with 20 s plasma pretreatment, 20 min UV irradiation, and 40 wt % VBV in water.

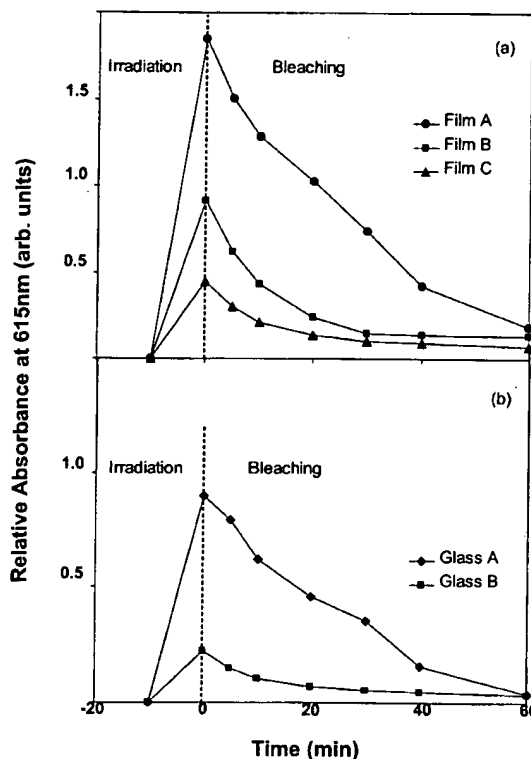


Figure 6. Response of (a) VBV-graft-copolymerized LDPE films and (b) VBV-graft-copolymerized glass to irradiation and the subsequent bleaching in air. The concentration of VBV solution used for the LDPE films A, B, and C is 40, 30, and 20 wt %, respectively, while that for the silanized glass A and B is 40 and 20 wt %, respectively. Argon plasma-pretreatment time of 20 s and UV-irradiation time of 20 min were used.

minus the absolute absorbance of the base spectrum. An increase in the amount of grafted VBV results in a corresponding increase in the number of viologen radical

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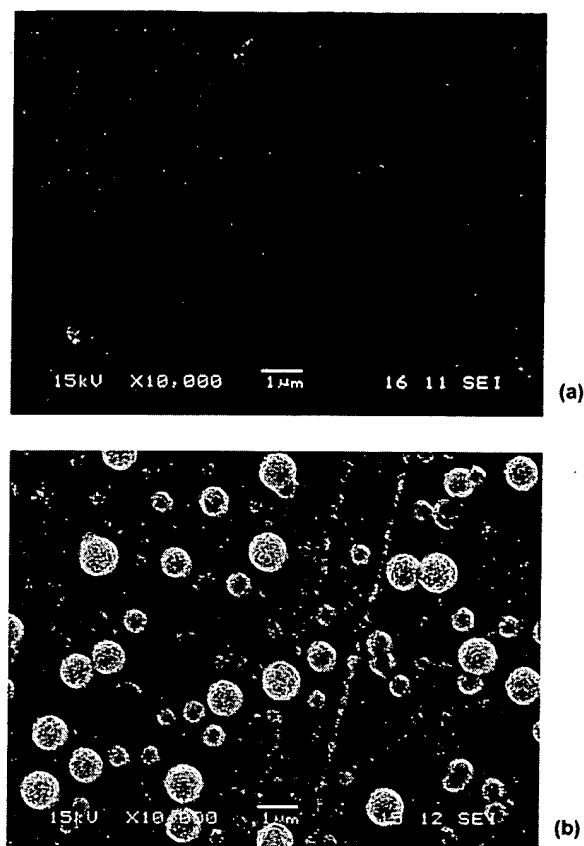


Figure 7. Scanning electron microscopy images of (a) VBV-graft-copolymerized LDPE film A and (b) viologen-graft-copolymerized LDPE made by the previous method.²⁵

cations formed (seen as an increase in relative absorbance at 0 min) and hence the time required for complete subsequent bleaching. The higher absorbance of film A compared to films B and C confirms the difference in the VBV graft concentration of these films. Thus, it is possible to control the amount of VBV graft copolymerized on the substrate by varying the VBV monomer concentration used.

The SEM images of VBV-graft-copolymerized LDPE film A and a viologen graft-copolymerized LDPE film made by the previous method,²⁵ which involves the initial graft copolymerization of VBC on LDPE film followed by reaction with 4,4'-bipyridine and dichloro-*p*-xylene to form viologen moieties, are compared in Figure 7. Figure 7a confirms the homogeneous nature of the VBV-graft-copolymerized LDPE surface. In contrast, spherical nodules of about 1 μm or less can be seen to be well distributed on the surface of the viologen-grafted LDPE film made by the previous method²⁵ (Figure 7b). The nodules arise from the VBC-graft copolymerization step and may be due to the formation of long chains of poly-(VBC) attached to active sites induced on the LDPE substrate during plasma pretreatment. The subsequent reaction with 4,4'-bipyridine and dichloro-*p*-xylene increases the size of the nodules but the distribution on the LDPE surface remains the same. In the present method, the VBV monomer has two vinyl groups. It can be expected that during the graft copolymerization process there would be extensive cross-linking between the growing chains. This cross-linking effect may give rise to a more even surface (Figure 7a) rather than the nodules seen in Figure 7b.

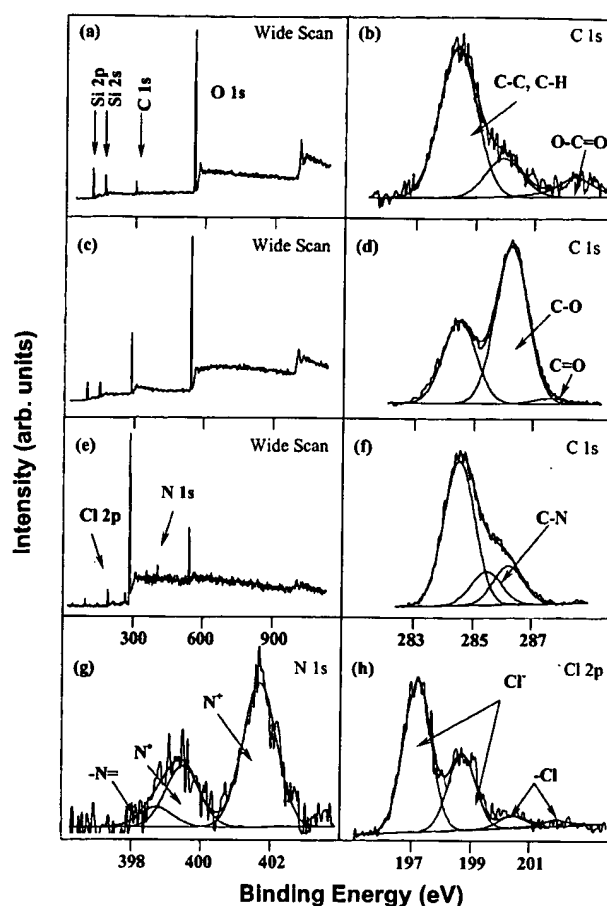


Figure 8. XPS wide-scan and C 1s core-level spectra of (a) and (b) pristine glass surface, (c) and (d) silanized glass surface, (e) and (f) VBV-graft-copolymerized silanized glass, and (g) N 1s and (h) Cl 2p core-level spectra of VBV-graft-copolymerized silanized glass. Graft copolymerization is carried out with 20 s plasma pretreatment, 20 min UV irradiation, and 40 wt % VBV in water.

When the present method is compared with the previous method,²⁵ there are obvious advantages. First, the grafting time is significantly reduced from 20 h to about 20 min and the temperature is reduced from 60 to 28 °C. Second, the solvent used in the present method is water instead of organic solvents (DMF, THF, etc.) which may affect some types of substrates during the prolonged treatment at relatively high temperature. Third, the graft-copolymerized films from the present method are more homogeneous, as UV-vis spectroscopy scans across the length of the films indicate that the absorbance at 400 nm changes by 1% or less. Finally, a higher graft concentration and relatively longer chain viologen units may be obtained in the present method. This would result in a higher concentration of viologen radical cations upon photoirradiation, and hence a stronger and longer lasting photoresponse will be generated.

3. VBV-Graft Copolymerization on Glass. The XPS wide-scan and C 1s core-level spectra of the pristine glass surface are shown in Figure 8a and 8b, respectively, while the corresponding spectra of the glass surface after GPS silanization (using 1 vol % of GPS) are shown in Figures 8c and 8d, respectively. The persistence of a residual C 1s core-level signal on the pristine glass surface is probably associated with the presence of adventitious carbon and hydrocarbons. The C 1s peak intensity in the wide-scan spectrum of the glass surface increases substantially after

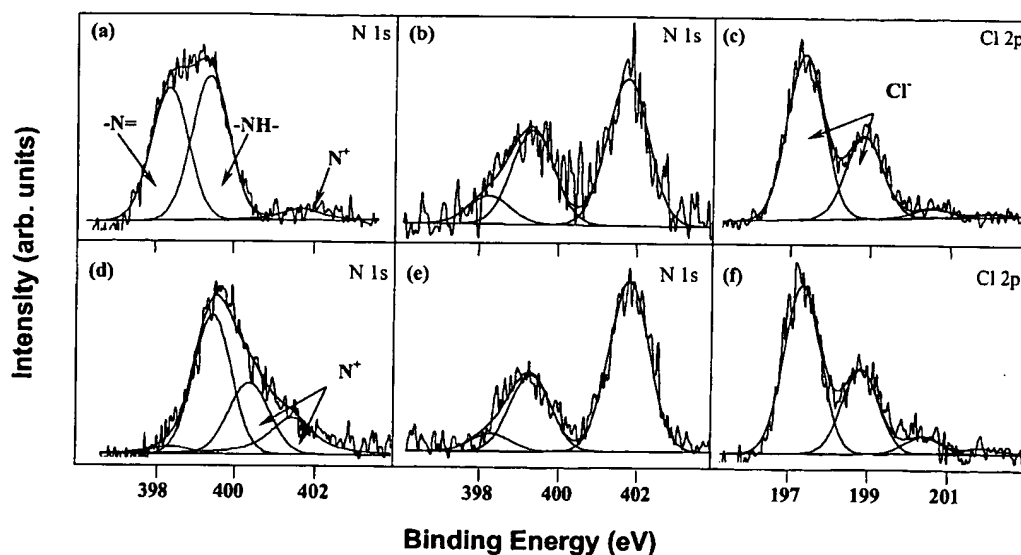


Figure 9. XPS core-level spectra of (a) pristine EM base film, (b) and (c) VBV-graft-copolymerized EM base film (after 20s plasma pretreatment), (d) pristine EM salt film, and (e) and (f) VBV-graft-copolymerized EM salt film. Graft copolymerization is carried out with 20 min UV irradiation and 40 wt % VBV in water for both the EM base and EM salt films.

GPS silanization (compare Figures 8a and 8c). The C–H/C–O peak area ratio of the silanized glass surface in Figure 8c is about 1:1.9, which is somewhat lower than the theoretical C–H/C–O ratio of 1:2 expected for the hydrolyzed and coupled GPS. This deviation probably has resulted, at least in part, from the presence of adventitious carbon and hydrocarbons on the pristine glass surface.

After the GPS-silanized glass surface is further functionalized through UV-induced surface graft copolymerization of VBV by the same method used in functionalization of LDPE surface, the surface compositions changed significantly, as shown in Figure 8e. In comparison with the spectrum shown in Figure 8c, a decrease in the intensities of O and Si, an increase in the intensity of C, and the emergence of N and Cl can be observed in Figure 8e, when the viologen layer is grafted onto the silanized glass surface. The presence of surface-grafted VBV is also indicated by the changes in line shapes of the C 1s core-level spectra after UV-induced graft polymerization with VBV (Figure 8f). There is an obvious decrease of intensity of C–O species and the emergence of the C–N species. Furthermore, the N 1s (Figure 8g) and Cl 2p core-level spectra (Figure 8h) also confirm the introduction of VBV species on the surface of silanized glass slides.

The pale yellow VBV-graft-copolymerized silanized glass slide surface turns dark blue under UV irradiation due to the formation of the viologen radical cation and bleaches upon termination of the irradiation and exposure to air. As shown in Figure 5b, the response of the VBV-graft-copolymerized glasses upon photoirradiation is similar to that of the VBV-graft-copolymerized LDPE films. Similarly, a higher VBV monomer concentration results in higher graft concentration on the silanized glass and a stronger photoresponse is observed (Figure 6b). When the relative absorbance of the VBV-graft-copolymerized LDPE surface is compared with that of VBV-graft-copolymerized silanized glass, the latter appears to be much lower. For example, the relative absorbance of VBV-grafted glass A at 615 nm is close to 1 while the relative absorbance of VBV-grafted LDPE film A at 615 nm is almost doubled. In both cases, identical grafting conditions were used, but since only one side of the glass slides was silanized and treated with VBV solution, its

photoresponse is correspondingly lower. The surface morphology of the VBV-graft-copolymerized silanized glass surface was also investigated by SEM, and the images are very similar to those of VBV-graft-copolymerized LDPE surfaces (Figure 7a), and we can conclude that VBV can be graft copolymerized in a homogeneous manner on the silanized glass surfaces.

In the previous method,²⁵ the introduction of viologen moieties onto the surface of glass was also attempted. The process involved reacting a GPS-silanized glass slide with 4-bromoaniline, in 2-propanol, at 60 °C for 6 h. The bromide group can then act as a site for the formation of viologens when the slide is reacted with 4,4'-bipyridine. Further reaction of the slide with an equimolar mixture of 4,4'-bipyridine and dichloro-*p*-xylene, at 60 °C, for 20 h, resulted in the silane layer turning yellowish brown. However, the silane layer was unstable and portions of it were washed away during the reaction period resulting in a nonhomogeneous surface.

4. VBV-Graft Copolymerization on PANI Films.

The surface compositions of pristine EM base film and VBV-graft-copolymerized EM base film as characterized by XPS spectra are shown in Figure 9. In pristine EM base film, the nitrogen species comprise mainly imine (–N=) and amine (–NH–) groups, corresponding to BEs at 398.2 and 399.4 eV, respectively. Only a small amount of nitrogen is in the N⁺ state with a BE > 400.8 eV corresponding to the presence of a small amount of oxidized species (Figure 9a). The [–NH–]/[–N=] ratio of 1.08 is consistent with the intrinsic redox state of the EM base form of PANI with equal proportions of imine and amine groups.⁴⁷ After the EM base film is graft copolymerized with VBV, it is clear that the imine (–N=) peak decreases and N⁺ becomes a prominent feature (Figure 9b). In this case, the imine group (–N=) could be attributed to the EM base as well as the unreacted pyridine group and the peak at 399.4 eV could be associated with amine group (–NH–) from the EM base as well as the viologen radical cation (N⁺) formed during X-ray excitation in the analysis chamber. Thus, although the N/C ratio determined by

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XPS analysis is 0.075 which is close to that expected for VBV, this value may not be taken as an indication of graft concentration since the EM base may contribute to the N and C signal if the VBV graft layer is less than the XPS probing depth. The Cl^- peak in the Cl 2p core-level spectrum (Figure 9c) can be taken as further evidence which confirms the presence of VBV on EM base film.

In the case of the EM salt film, the VBV-graft copolymerization can be successfully carried out without the plasma-pretreatment step. The N 1s core-level spectrum of pristine EM salt film is shown in Figure 9d. The high $[\text{N}^+]/[\text{N}]$ ratio (0.47) indicates a highly conductive film, and the conductivity is measured to be about 5 S/cm. After successful graft copolymerization with VBV (as shown in Figures 9e and 9f), the surface resistance is expected to increase since the VBV graft layer is nonconductive. After the EM salt film is extracted from the quartz plates and before it is washed with water, the surface resistance on the side without VBV is $10^5 \Omega/\text{sq}$ and that of the side with the VBV graft copolymer is $10^7 \Omega/\text{sq}$. After washing with doubly distilled water to remove the unreacted VBV, the surface resistance of the side of the EM salt film without VBV graft copolymer increases to $10^6 \Omega/\text{sq}$ which indicates that a certain extent of deprotonation has occurred during the washing process.

An alternative method to prepare conductive EM film which is graft copolymerized with VBV is the reprotonation of the VBV-graft-copolymerized EM base film. The surface resistance of the pristine EM base film is more than $10^{10} \Omega/\text{sq}$. After graft copolymerization, the surface resistance of EM base film on the side with the VBV graft copolymer is about $10^8 \Omega/\text{sq}$. After immersion in 1 M HClO_4 or HCl for 24 h, the EM base film is reprotonated and the surface resistance of the EM film on the side without VBV decreases to $10^3 \Omega/\text{sq}$ (corresponding conductivity is 0.5 S/cm, based on a thickness of 20 μm) while the surface resistance of the VBV-graft-copolymerized side remains at $10^8 \Omega/\text{sq}$ which is similar to that of VBV-graft-copolymerized LDPE film. The surface resistances of the VBV-graft-copolymerized side do not change much when the graft copolymerization is carried out at different concentrations of VBV solution ranging from 20 to 40 wt %. Furthermore, the two-probe or four-probe measurements taken at three points or more on the films indicate a variation of less than 10%. This suggests that a

concentration of 20 wt % is adequate for the formation of a homogeneous layer of VBV on the surface of the EM substrate.

The conductivity of the EM film makes it possible for use in bioaffinity sensors since conducting electroactive polymers (CEPs) have been demonstrated to have remarkable sensing applications through their ability to be reversibly oxidized or reduced by applying electrical potentials.⁴⁸ CEPs have been used to immobilize several biological species, including enzymes, antibodies, and haptens, as well as generate rapid analytical signals.⁴⁸ At the same time, viologen derivatives are most commonly used for the electron transfer from the electrode surface to the active sites of biomaterials.¹⁷ The application of the VBV-graft-copolymerized EM films as biosensors would be further explored in the future.

Conclusion

The vinyl group containing viologen, 1,1'-bis(4-vinylbenzyl)-4,4'-bipyridinium dichloride (VBV), was successfully synthesized and graft copolymerized on argon plasma-pretreated LDPE, silanized glass, and polyaniline films. The surface composition and microstructure of the graft-copolymerized substrate surface were characterized by XPS, UV-vis absorption spectroscopy, and scanning electron microscopy (SEM). The amount of viologen grafted depends on the plasma-pretreatment time of the substrate, the UV-induced graft copolymerization time, and the monomer concentration. Compared with a previously reported technique, this method offers the following advantages: it significantly reduces the time required for graft copolymerization as well as the reaction temperature, it can be more widely used because the solvent used is water instead of organic solvent, and it produces a homogeneous graft layer on the substrate. The response of the VBV-graft-copolymerized LDPE films and VBV-graft-copolymerized silanized glass to photoirradiation and subsequent bleaching in air has been demonstrated. Electrically conductive VBV-graft-copolymerized polyaniline film can be prepared by this method, and such films have the potential for applications as electrodes and sensing materials.

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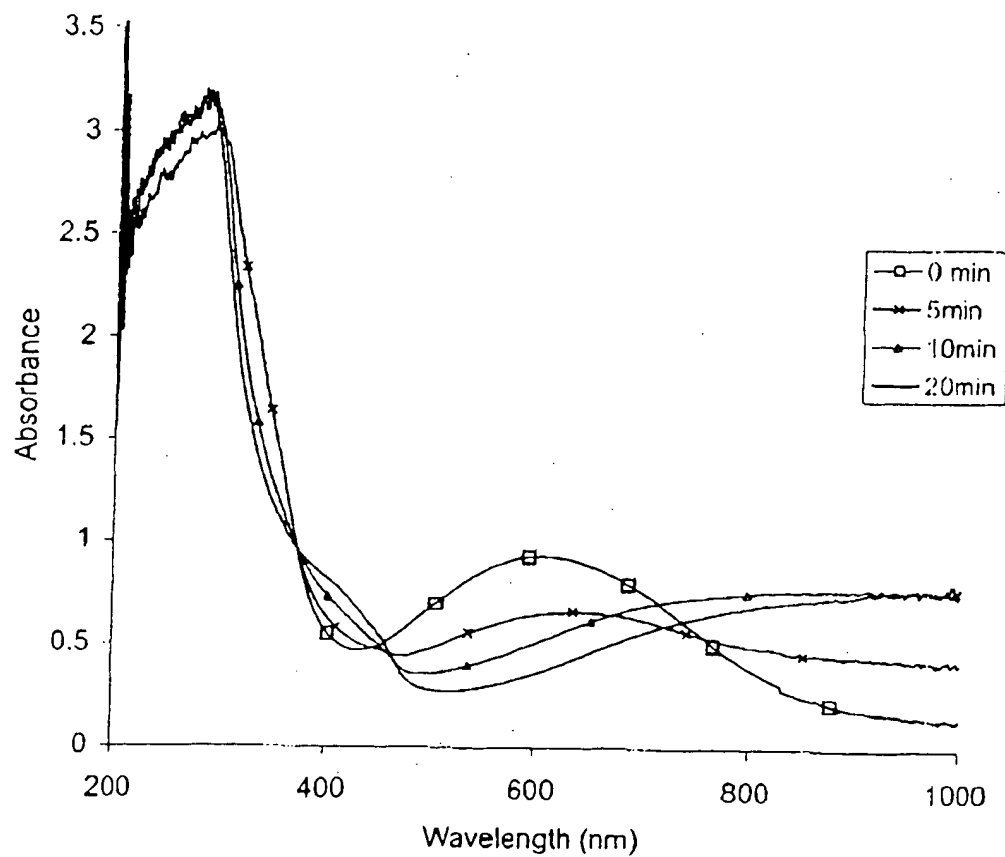


Fig. 2

